

Innovative developments in the selective removal and reuse of heavy metals from wastewaters

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Abstract Sulphide precipitation of heavy metal containing wastewaters results in low effluent concentrations. However, sulphide precipitation is not widely applied in practice because the dosing of sulphide cannot adequately be controlled. A new process was developed where the combination of a sulphide-selective electrode (pS-electrode) and pH electrode controls the sulphide addition. Precipitation experiments were performed on a laboratory-scale in batch and continuous reactor systems with synthetic wastewaters containing Cd, Cu, Ni, Pb or Zn. The response of the pS-electrode during precipitation was unique for each heavy metal and was directly related to the solubility product of the corresponding metal sulphide. The metals were removed to levels $<0.05 \text{ mg.l}^{-1}$ at pH 6.0 by sulphide precipitation while maintaining a total sulphide concentration $<0.02 \text{ mg.l}^{-1}$. By the control of pS at different levels and keeping the pH constant at 6.0, the metals in solutions of both Cu and Zn could be precipitated selectively from solution in a batch and continuous reactors. The use of a membrane reactor in combination with control of pH and pS offers a simple, cheap, efficient and sustainable technique with respect to obtaining very low effluent concentrations and selective removal of metals as pure metal sulphides which can be reused.

Keywords Metal; microfiltration; selectivity; sulphide precipitation; wastewater

Introduction

Industrial activities in the past have led to severe heavy metal contamination of groundwater. Metal pollution still continues with the discharge of industrial wastewaters from metal processing, metal finishing and plating industries and acidic mine drainage waters (Patterson, 1990). There are numerous treatment technologies for the removal of heavy metals from wastewater including precipitation, coagulation–flocculation, ion exchange, solvent extraction, complexation, adsorption, filtration and membrane processes (Peters *et al.*, 1984; Brooks, 1991). Most of these treatment technologies produce concentrated sludges that are then stored in controlled hazardous waste disposal sites. A more sustainable solution for heavy metals in wastewaters could be obtained if treatment processes focus on recovery and reuse of the metals as it is also the reserves of metals that are depleting (Patterson, 1990). Reuse of metals can only become economically and technically feasible when metals are removed selectively and pure metal sludges are produced. Besides, there is also an increasing need for treatment systems able to achieve very low effluent concentrations.

In industry, by far the most widely used treatment process for wastewater is precipitation. Hydroxide precipitation is most popular due to its relative simplicity, low costs and ease of automatic pH control (Peters *et al.*, 1984). However, sulphide precipitation is superior over hydroxide precipitation as: (a) effluent concentrations are orders of magnitude lower ($\mu\text{g l}^{-1}$ versus mg l^{-1}); (b) the interference of chelating agents in the wastewater are less problematic; (c) precipitation gives improved selectivity; (d) high reaction rates result in low hydraulic retention times; (e) metal sulphides exhibit better thickening and dewatering characteristics than corresponding hydroxide sludges; and (f) sulphide precipitates can be processed by existing smelters for metal recovery (Kim and Amodeo, 1983;

Peters and Ku, 1987). The sulphide precipitation processes can be achieved using different sulphide sources: soluble (Na_2S , NaHS), slightly soluble (CaS), insoluble (FeS) and gaseous (H_2S). However, sulphide precipitation also has some potential disadvantages, which have to be considered. If the amount of sulphide reagent is not added in stoichiometric quantities with respect to the amount of metals, either excess metals or excess sulphide will remain in solution. Besides, precipitation by sulphide may result in colloidal metal sulphide precipitates that can poorly be separated from the water phase by solid-liquid separation processes such as sedimentation or filtration (Peters and Ku, 1987).

This paper discusses laboratory-scale research into the selective removal of heavy metals from wastewater by sulphide precipitation. The sulphide addition can be controlled by online measuring the sulphide concentration in solution by a sulphide (S^{2-}) ion-selective electrode (pS electrode) analogous to the measurement and control of pH (Schmidt *et al.*, 1994). Because the electrode to monitor the sulphide concentration is essential, the application of this method will be discussed first. The pS electrode in combination with the pH electrode was applied for batch and continuous precipitation focussing on both selective precipitation and achieving low metal and sulphide concentrations. A removal technology was designed and tested on a bench-scale system where sulphide precipitation was controlled by using pH and pS electrodes and ultrafiltration membranes where applied to separate the precipitate efficiently.

Materials and methods

Sulphide (S^{2-}) ion-selective electrode (pS-electrode)

A solid state AgS electrode was used to monitor S^{2-} in heavy metal containing wastewaters for control of sulphide addition (Schmidt *et al.*, 1994). The electromotive force of the electrode system, a pS-electrode (MicroScale Measurement, The Netherlands) and double junction reference electrode (Schott Geräte, Germany) is related to the activity of fully dissociated sulphide (S^{2-}) and is described by the Nernst equation (Amman, 1986):

$$E = I + H \log (\text{S}^{2-}) \quad (1)$$

where I is the intercept and H is the slope of the electrode response. The pS-electrode was calibrated with a solution of 10 mM Na_2S that was titrated with 0.1 M HNO_3 from high to low pH values. Solution pH was measured by a combined glass electrode (Schott Geräte, Germany) which was calibrated with pH buffers 4.0 and 7.0 (Merck, Germany). The sulphide activity is related to the total sulphide concentration ($S_{\text{TOT}} = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}]$) and pH according to:

$$(\text{S}^{2-}) = \frac{S_{\text{TOT}}}{1 + [(\text{H}^+) / K_{\text{A1}}] + [(\text{H}^+)^2 / K_{\text{A1}}K_{\text{A2}}]} \quad (2)$$

where (H^+) is the proton activity as measured by a glass electrode, K_{A1} is the first dissociation constant of hydrogen sulphide ($\text{H}_2\text{S} \leftrightarrow \text{H}^+ + \text{HS}^-$) and K_{A2} is the second dissociation constant of hydrogen sulphide ($\text{HS}^- \leftrightarrow \text{H}^+ + \text{S}^{2-}$). Figure 1 shows the electromotive force as a function of pS; in analogy to pH measurements the term pS is introduced, $\text{pS} = -\log(\text{S}^{2-})$. The pS electrode behaves perfectly according to the Nernst equation ($R^2 = 0.999$) for the measured range. The electromotive force E (mV) can be directly converted to pS units, applying Eq. (1).

Precipitation experiments in batch and continuous stirred tank reactor (CSTR)

The CSTR experiments were performed in a 1,000 ml glass vessel with four baffles, which

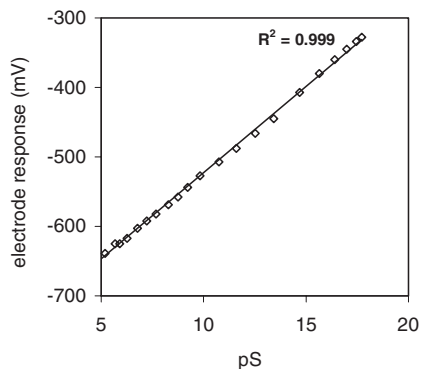


Figure 1 Electromotive force of the electrode system as a function of pS

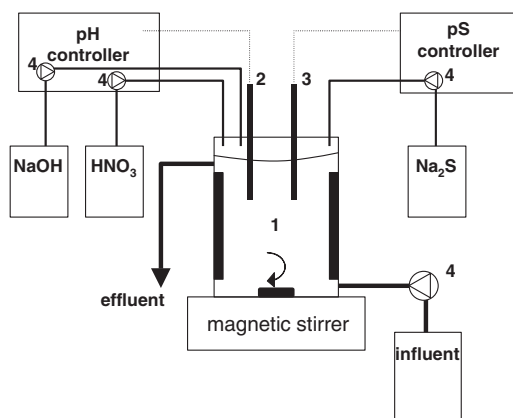


Figure 2 Schematic presentation of the experimental set-up for batch and CSTR experiments (1: reactor; 2: pH-electrode; 3: pS-electrode; 4: peristaltic pumps)

was ideally mixed by a magnetic stirrer and operated at room temperature (Figure 2). The pH- and pS-electrodes were connected to proportionally integrated controllers (Endress + Hauser, Germany) and equipped with stock solutions of HNO_3/NaOH and Na_2S , respectively, to control pH and pS levels in the reactor. The stock solutions of NaOH and Na_2S were provided with $\text{Ca}(\text{OH})_2$ pellet columns to prevent absorption of CO_2 into the solution. The pS and pH-controllers were connected to an automatic data logging system (Data Electronics Ltd., Australia) to record pH and pS online. The batch experiments were performed with the same experimental set-up, except that the inlet and outlet were closed.

For the batch precipitation experiments, monometal solutions of approximately 1 mM and 3 mM of $\text{Me}(\text{NO}_3)_2$ salts ($\text{Me} = \text{Cd}, \text{Cu}, \text{Ni}, \text{Pb}, \text{Zn}$) were titrated by hand with 100 mM Na_2S . The pH was controlled at 6.0 by the pH-controller. After constant readings of pH and pS, the next aliquot of Na_2S was added. The titration was ended after reaching the equivalence point (EP); this is the point where the metal is almost completely precipitated and pS starts to drop drastically (see Figure 3). The pS and pH were recorded online and periodically 5–10 ml samples were taken from the reactor for metal analysis. The samples were filtered through 0.45 μm membranes (Schleicher & Schuell, Germany) and the filtrate was acidified to 0.1 M HNO_3 and stored at 4°C until analysis by ICP-AES. A batch titration experiment was performed with a mixture of Cu and Zn (7 and 10 mM) at pH 6.0 to study the selective precipitation of the metals.

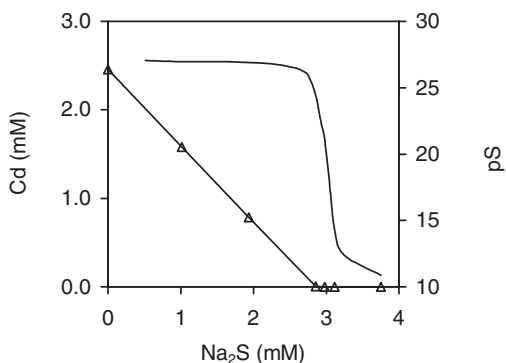


Figure 3 Batch titrations of 3 mM $\text{Cd}(\text{NO}_3)_2$ with 100 mM Na_2S at pH 6.0. Note that the triangles denoted Cd concentrations and solid lines denote pS

CSTR experiments were performed with monometal solutions of $\text{Me}(\text{NO}_3)_2$ salts at pH 6.0 and pS 15.0. This condition corresponds to a total sulphide concentration S_{TOT} of 0.03 mg l^{-1} as calculated by Eq. (1). Experiments were performed at hydraulic retention times (HRT) of 1, 5 and 30 minutes for Cu, Pb and Zn and at 30 minutes for Cd and Ni. The metal load rate was kept constant at 0.25 mM min^{-1} . The experiments were run for 10–15 HRTs. The effluent of the reactor was sampled 1–2 times per HRT, the samples were filtered through $0.45 \mu\text{m}$ membranes, the filtrate was acidified to 0.1 M HNO_3 and stored at 4°C until analysis by ICP-AES. The selective precipitation of heavy metals was studied for a mixture of Cu and Zn (3.8 mM each) at pH 6.0 at various pS levels at a HRT of 30 minutes. The pS was maintained at a constant level for 3–4 HRTs and Cu and Zn in the effluent were periodically measured. Precipitation of Zn in CSTR was studied extensively at a HRT of 30 minutes, influent concentration of $76 \text{ mM Zn}(\text{NO}_3)_2$, pH 6.5 and various pS levels. Each experiment at constant pS was run for 4–6 hours, corresponding to 8–10 HRT.

Results and discussion

Batch monometal experiments

The pS and the metal concentration during the titration of a solution with an initial Cd concentration of 3 mM are shown in Figure 3.

All batch titrations (Cd, Cu, Ni, Pb and Zn) showed a typical pS response which can be divided into two regions: before and after the equivalence point, EP. Before the EP, pS remains constant at an almost constant level which was characteristic for each metal. After the EP, when the metal is completely precipitated, the electrode response is dictated by the dissolved sulphide in solution. The metal concentration at the EP was for all metals $<0.05 \text{ mg l}^{-1}$ (detection limit of ICP-AES). The characteristic pS level before the equivalence point is determined by the solubility product of the metal sulphide. The solubility product (K_{SP}) of a metal sulphide (MeS) is given by:

$$K_{\text{SP}} = (\text{Me}^{2+})(\text{S}^{2-}) \quad (3)$$

where (Me^{2+}) is the equilibrium activity of metal ion Me^{2+} and (S^{2-}) is the equilibrium activity of S^{2-} . The activity of S^{2-} is directly measured by the pS-electrode. The metal concentration $[\text{Me}^{2+}]$ as measured by ICP-AES has to be converted to activity by (Stumm and Morgan, 1996):

$$(\text{Me}^{2+}) = \gamma_{\text{Me}} [\text{Me}^{2+}] \quad (4)$$

where $[Me^{2+}]$ is the concentration of the metal ion (M), (Me^{2+}) is the activity of the metal ion (M) and γ_{Me} is the activity coefficient of the metal ion. The activity coefficient can be calculated by the Davies equation (Stumm and Morgan, 1996). Each metal had a characteristic pS level before the EP (Cd: 27.5–28.5, Cu: 39.5–40.5, Pb: 28.5–29.5 and Zn: 18.5–19.5). The pS level dropped slightly during the titrations (see Figure 3 for Cd) as the metal concentration drops and, at the same time, $(Me^{2+})(S^{2-})$ has to remain constant according to Eq. (4). The average $\log(K_{SP})$ value for the experiments at 1 and 3 mM are given in Table 1, together with the literature values of stability constants for metal sulphide precipitates.

The values from the experiments are in same order of magnitude as the literature data but there is some discrepancy as is also the case for the literature data. This is mainly the result of differences in experimental conditions (e.g. mixing intensity, supersaturation, solids concentration, reaction time) which result in different types of precipitates with different solubility products (Daskalakis and Helz, 1993; Jones *et al.*, 1996). The measured solubility products should therefore be regarded as conditional K_{SP} s and in dynamic situations, e.g. treatment of metal containing wastewaters, metastable precipitates may control solubility (Daskalakis and Helz, 1992).

Continuous monometal experiments

The pH and pS level were controlled at 6.0 ± 0.2 and 15.0 ± 0.3 , respectively, throughout the experiments. Figure 4 shows the average effluent concentrations over the last period (1–2 hours) of the runs. The effluent concentration appears to be independent of the hydraulic retention time for both Pb and Zn, but Cu shows a strong dependent effect. The effluent concentrations for Cd, Pb and Zn were in the range of the detection limit of ICP-AES ($<0.05 \text{ mg l}^{-1}$). However, Cu and Ni showed higher levels even for a HRT of 30 minutes indicating that the precipitation reaction was slow or that metal sulphide

Table 1 Comparison of experimental $\log K_{SP}$ at 1 and 3 mM and literature data

Metal	1 mM	3 mM	Literature data ¹
Cd	-28.8 ± 0.3	-29.8 ± 0.6	-25.8, -28.2 ²
Cu	-41.5 ± 0.5	-41.0 ± 0.3	-36.1 (CuS), -48.5 (Cu ₂ S)
Ni	-26.0 ± 0.9	-25 ± 2	-19.4 (α), -24.9 (β), -26.6 (γ)
Pb	-30.6 ± 0.9	-30.8 ± 0.4	-27.5
Zn	-20.9 ± 0.3	-22.1 ± 0.3	-22.5 (α), -24.5(β), -18.4 ³

¹Smith and Martell (1976); except ²Daskalakis and Helz (1992) and ³Daskalakis and Helz (1993)

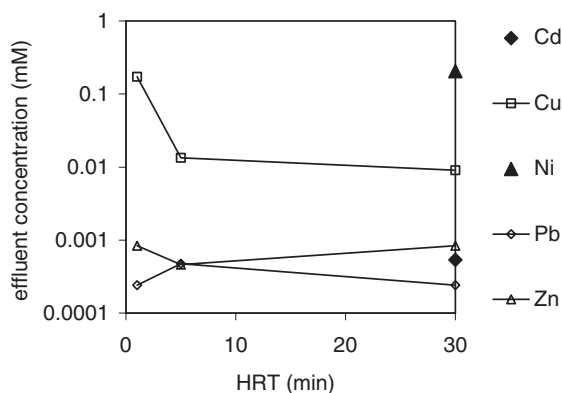


Figure 4 Effluent metal concentration (Cd, Cu, Ni, Pb and Zn) as a function of the hydraulic retention time in CSTR precipitation experiments at pH 6.0

particles smaller than 0.45 μm were produced. The presence of metal sulphide particles in the filtrates was visually observed for Cu but not for Ni.

The precipitation of Zn in CSTR was studied in more detail at different pS levels. It was observed that when S^{2-} and Zn^{2+} are present at stoichiometric ratios, the concentration of soluble Zn is at its minimum. At lower pS levels, an overdose sulphide is present and Zn again increases. This is due to the formation of soluble sulphide complexes $\text{Zn}(\text{HS})^+$ and $\text{Zn}(\text{HS})_2^0$ (Daskalakis and Helz, 1992). Precipitation of ZnS at pH 6.5 can best be performed at a pS level of 15–16 where a very low zinc concentration ($<0.05 \text{ mg l}^{-1}$) is accompanied by a negligible total sulphide concentration ($<10 \mu\text{g l}^{-1}$).

Selective precipitation of Cu-Zn mixtures

As the response of the pS-electrode is directly coupled to the solubility product of the metal sulphide precipitate and pS and pH level can be controlled accurately, we have a control parameter to selectively precipitate heavy metals. Figure 5 shows the metal concentrations and pS during both the batch titration and CSTR experiments for a solution of Cu and Zn.

For the batch titration, the metals are precipitated consecutively: first the metal with the lower solubility (Cu) and then Zn (see Table 1). Both titrations showed two constant pS-levels during precipitation, again showing that the levels of pS during precipitation were unique for every heavy metal. The selectivity of precipitation is 100% for Cu and Zn. The experiment was repeated for a Cu-Zn solution in CSTR at pH 6.0 and control of pS at various levels (control of both pH and pS within 0.2 units). The average Cu and Zn concentration in the effluent as function of pS are shown in Figure 5. Also in CSTR, 100% selective precipitation of Cu and Zn was reached in the pS range 30–37. Thus, by a sequential precipitation in two steps where both reactors are controlled at different pS levels, both Cu and Zn can be precipitated in pure form which increases the possibilities of reuse of the produced metal sulphide sludges. The selectivity of the precipitation will depend upon the differences in solubility product. However, differences in the rate of the precipitation reaction can also possibly be applied for selective precipitation, e.g. Ni shows much slower kinetics than Cd, Pb and Zn (see Figure 4).

Design for full-scale plant

Based on the experiments in batch and CSTR, a membrane precipitation system was designed as shown in Figure 6 and tested with both ultrafiltration (pore size of 0.01 μm) and microfiltration (0.1 μm) membranes for the precipitation of Zn. By controlling pS at very low levels with the pS-electrode and by offering a high specific surface for crystal growth, local supersaturation can be minimised and therefore large particles can be produced in a

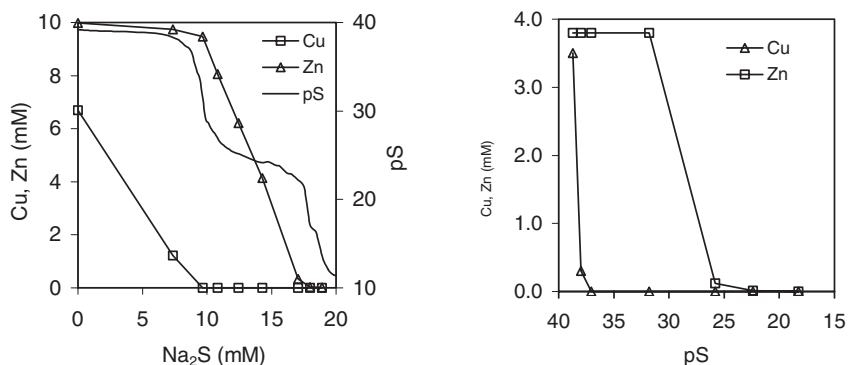


Figure 5 Selective precipitation at pH 6.0 for a mixture of Cu and Zn in batch (left) and CSTR (right) precipitation experiments

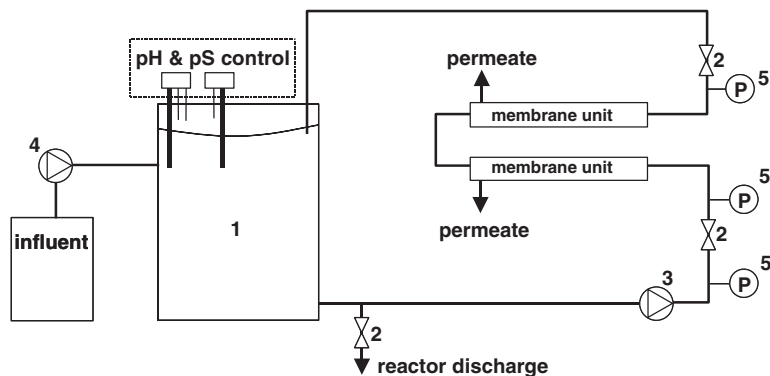


Figure 6 Schematic presentation of the membrane precipitation reactor (1: reactor; 2: ball valves; 3: centrifugal pump; 4: peristaltic pump; 5: pressure gauges)

membrane reactor (Jones *et al.*, 1996). These large particles are easily separated from the liquid by using membranes with large pore sizes, resulting in very high permeate fluxes and thus low costs.

This concept was confirmed by the measured high permeate fluxes for ZnS even at very high total solids contents up to 200 g l^{-1} . The membrane reactor was run for six days at a ZnS content of 60 g l^{-1} without fouling of both UF and MF membranes. The measured Zn concentration in the permeate was below the detection of ICP-AES ($<0.05 \text{ mg l}^{-1}$). This is in accordance with the batch and continuous experiments and showed that ZnS was completely retained by the membrane filter.

Conclusions

Sulfide precipitation in combination with control by pH and pS electrodes, control of the residence time HRT, and separation of the precipitate by means of microfiltration membranes, offers a simple, cheap, efficient and sustainable technique with respect to:

- obtaining very low effluent concentrations;
- selective removal of metals as pure metal sulphides which can be reused.

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